

A 19, 1.40



Issued November 30, 1909.

U. S. DEPARTMENT OF AGRICULTURE,  
BUREAU OF PLANT INDUSTRY—Circular No. 40.  
B. T. GALLOWAY, Chief of Bureau.

---

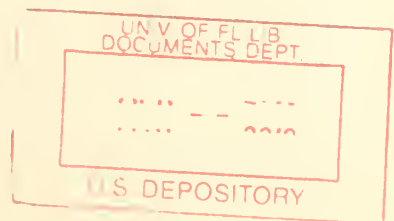
## A SIMPLE METHOD OF DETECTING SULPHURED BARLEY AND OATS.

---

BY  
W. P. CARROLL,  
ASSISTANT IN CHARGE OF THE CHICAGO GRAIN  
STANDARDIZATION LABORATORY.

---

WASHINGTON : GOVERNMENT PRINTING OFFICE : 1909



## BUREAU OF PLANT INDUSTRY.

---

*Chief of Bureau,* BEVERLY T. GALLOWAY.

*Assistant Chief of Bureau,* ALBERT F. WOODS.

*Editor,* J. E. ROCKWELL.

*Chief Clerk,* JAMES E. JONES.

[Cir. 40]

# A SIMPLE METHOD OF DETECTING SULPHURED BARLEY AND OATS.

## INTRODUCTION.

For years it has been the common practice in some grain centers to subject stained or discolored barley and oats to a process of bleaching in order to remove, or at least partially remove, the discoloration and to a certain extent improve the appearance of kernels otherwise damaged. The common agent to accomplish this result is sulphur in the form of sulphurous acid, and the process itself is known by different names, among which are the terms "sulphuring," "bleaching," and "purifying."

The general appearance, especially the color, of barley and oats, has an important bearing in determining their commercial grades and values, and in view of the fact that the bleaching of these grains has become common, and because it is oftentimes difficult to discriminate between grain that has been bleached and grain that is naturally bright in appearance, it was deemed expedient to use a simple qualitative method by means of which the grain merchant or grain inspector could determine whether or not grain has been sulphured. Heretofore the sense of smell or the personal judgment has been the only means available to practical grain men of differentiating between the natural and the bleached grains.

## METHOD OF BLEACHING USED.

Sulphur burned in air or in the presence of oxygen becomes sulphur dioxide, a colorless, transparent gas with a sharp, pungent odor similar to that found in burning sulphur matches. This gas is very soluble in water, forming sulphurous acid, which is the bleaching agent for barley and oats.

In actual practice, the sulphur is changed to sulphur dioxide by burning in an oven, from which the fumes are conducted to a receptacle or bleaching tower, from the bottom to the top of which the gas circulates, coming in contact with the grain that is constantly passing through the tower. Water must be supplied to change the dioxide into sulphurous acid, as sulphur dioxide is not a bleaching agent. This is

done by dampening the grain either with steam or small sprays of water playing upon the grain as it enters the tower.

The bleaching is supposedly brought about by the acid abstracting oxygen from the coloring matter of the grain. Complete bleaching is not immediate, and the grain is therefore conveyed in a damp condition from the bleaching apparatus to moderately air-tight bins, where it is allowed to remain long enough to finish the process. To prevent heating and to put the grain in a proper condition for shipping, it is moved about after some time in such a manner as will permit the air to pass freely through it, which to a certain extent will remove the acid odor but will not completely remove all of the sulphurous acid, the presence of which will always betray the fact that the grain has been "sulphured."

The method outlined in this circular for the detection of sulphurous acid has been one of the standard methods of ascertaining the presence of sulphurous acid in grain for several years, and a more detailed description of the chemical reactions that take place may be found in any of the later standard text-books on qualitative chemistry. The principle upon which the method is based is to change sulphurous acid into hydrogen sulphid, which in the presence of lead salt will give a brownish black precipitate. This method has been used in Germany for some years in detecting sulphurous acid in bleached seeds, and in modified forms by chemists in this country for similar purposes. In order to accelerate the test and at the same time reduce the possibility of error to a minimum, so that it can be used by persons other than those familiar with chemical reactions, it has been deemed advisable to make a few changes in the apparatus commonly used.

#### THE CHEMICALS NECESSARY FOR DETECTING SULPHURED GRAIN.

For the detection of sulphured grain a supply of chemically pure zinc, hydrochloric acid, lead acetate, ferric or platinic chlorid, and distilled water should always be on hand. The hydrochloric acid should be diluted to about 20 per cent of its normal strength by adding 4 parts of distilled water to 1 part of acid. The lead acetate must be dissolved in water, and to give the best results the solution is prepared by adding 2 grams of the acetate for every 98 cubic centimeters of distilled water, which makes practically a 2 per cent solution.

If the operator desires to make several tests, stock solutions of the proper strength should be made up in quantity. However, if the stock solution of lead acetate is allowed to stand very long it will become scummy and flakes will adhere to the sides of the container. Therefore, it will be necessary to filter it occasionally so that a clear, transparent liquid may always be ready for use when needed.

METHOD OF TESTING GRAIN.<sup>a</sup>

To perform the test, 10 grams of chemically pure, mossy, granular, or shot zinc are distributed over the bottom of a glass container with a capacity of at least 500 cubic centimeters. Upon the zinc are placed about 100 grams of the grain to be tested. Into the flask is poured enough dilute hydrochloric acid to cover the grain, approximately 100 cubic centimeters. The flask is then closed with a cork stopper provided with an inverted "L" glass tube about 7 millimeters in internal diameter. The short arm of the glass tube should project approximately one-half inch below the bottom of the stopper, while the long arm should extend nearly to the bottom of the test tube containing a 2 per cent solution of lead acetate. (See fig. 1.) A test tube of about 15 cubic centimeters capacity is large enough for this purpose and should not be over two-thirds full; otherwise the contents will spill



FIG. 1.—Chemicals and apparatus used for detecting sulphured grain.

over as soon as the gas begins to pass freely from the zinc and the hydrochloric acid. If the zinc is very pure—that is to say, free from all foreign substances—the action between the zinc and the hydrochloric acid will be retarded, but it may be considerably hastened by the addition of a few drops of ferric chlorid. On the left in figure 1

<sup>a</sup> In Bulletin 107 (revised), Bureau of Chemistry, U. S. Dept. of Agriculture, p. 187, the use of a lead salt in a little different form is recommended for the detection of sulphurous acid in vegetables. This test is commonly known as the lead-paper test and differs from the solution test described in this circular in that a piece of bibulous paper is saturated with a solution of a lead salt and is then placed underneath the stopper of the flask in which the hydrogen is generated instead of using the lead solution in a separate compartment. The lead-paper test has been used by some chemists for the detection of sulphurous acid in grain, and it was also tried in the Bureau of Plant Industry for the same purpose, but after repeated trials it was not deemed advisable to recommend its use by persons unfamiliar with chemical reactions.

are shown two flasks with connections to the test tubes. This figure fully demonstrates how the apparatus is to be adjusted.

When the hydrochloric acid comes in contact with the zinc in the bottom of the flask, hydrogen is liberated and bubbles may be noticed passing up through the grain and then through the lead acetate in the test tube. As soon as the air has been expelled from the flask, these bubbles are either hydrogen or hydrogen sulphid, conditional upon whether the grain is natural or sulphured. With unbleached grain the gas is hydrogen and the bubbles passing through the lead acetate solution will leave the liquid in the tube clear, colorless, and transparent, but with sulphured grain these bubbles will be hydrogen sulphid gas, which produces a brownish black, flocculent precipitate in the lead acetate. This precipitate is lead sulphid, caused by the breaking up of the hydrogen sulphid and the lead acetate, the lead of the latter uniting with the sulphur of the former.

Occasionally fine granules will be seen held in suspension in the lead acetate should the grain be very dusty, and the same conditions will exist if the acid is too strong, because strong acid produces violent action in the flask, which may cause to be carried over some fine particles of dust or zinc. These granules must not be mistaken for lead sulphid. After the operator has had a little experience he can readily distinguish the granules from the black, flocculent precipitate. It is easy to test these granules by adding a few drops of ferric chlorid (one part of ferric chlorid dissolved in ten parts of distilled water) to the precipitate in the test tube. If the precipitate is lead sulphid it will readily dissolve in the ferric chlorid, whereas the zinc particles and dust will remain practically unchanged. These particles and their consequent annoyance may be obviated to a great extent by screening the grain before it is put into the flask. A still better way, however, to circumvent this difficulty is to place a piece of clean absorbent cotton in the neck of the flask just below the outlet in the stopper, which will serve as a filter and allow the gas to pass through freely, but will retain any solid impurities that may come in contact with it.

#### NECESSITY FOR CLEANLINESS.

In all cases mixing pans, glassware, and all other apparatus should be clean, and no chemicals should be used that are not chemically pure. These precautions can not be urged or impressed too strongly upon the operator, because other substances might be present in the glassware and chemicals that would perhaps give a reaction similar to that of sulphurous acid. Rubber stoppers contain sulphur in their composition, although not in such a form that it is readily changed to hydrogen sulphid; still, it is advisable to use cork stoppers to avoid any possibility of doubt or controversy. Flasks with ground-glass stoppers, provided with special conducting tubes, are to be preferred in all cases where they are procurable.



## TESTS OF NATURAL BARLEY IN COMPARISON WITH SULPHURED BARLEY.

There seems to be a difference of opinion among persons engaged in the grain trade as to whether the precipitate of lead sulphid is procured only from grain that has been sulphured. Some contend that the natural sulphur found in barley rich in protein will give the same precipitate as that found in sulphured barley and furthermore that different soils will produce barley some of which will show a sulphur reaction. It may be said, however, in this connection, that the natural sulphur found in the protein of 200 or 300 grams of barley is too small to manifest itself in such a test, because the dilute acid has hardly sufficient time to penetrate the interior of the kernels. Moreover, facts do not bear out these contentions, as will be demonstrated.

To ascertain how barley grown on different soils and in different sections of the country would respond when subjected to the test described



FIG. 2.—Eight bottles filled with solutions, showing the results of tests of sulphured commercial barley (A) and of pure unsulphured barley (B) received from the agricultural experiment stations of Minnesota, Nebraska, Iowa, Wisconsin, Utah, Kansas, and Indiana.

in this circular, requests were made to the agricultural experiment stations of Minnesota, Nebraska, Iowa, Wisconsin, Utah, Kansas, and Indiana for barley samples that were known to be unsulphured. Each of these stations forwarded samples and a qualitative test of each was made. Four ounces of lead acetate were used instead of 10 cubic centimeters, 1,000 grams of barley were substituted for 100 grams in each case, and the acid and zinc were increased in the same proportion.

In figure 2 the solution in the bottle on the left is of inky blackness in color, indicating a heavy precipitate of lead sulphid. The barley which caused this discoloration was known to be sulphured. The hydrogen which passed through the solutions of the remaining seven bottles was generated in the presence of the natural barley from Minnesota, Nebraska, Iowa, Wisconsin, Utah, Kansas, and Indiana, respectively, but the liquid remained clear and transparent.

The bottle marked *A* on the left in figure 3 shows the result obtained by generating hydrogen in the presence of commercially sulphured barley and allowing the gas to pass through a solution of lead acetate, as in the qualitative test herein described. The bottles marked *B'*, *C'*, and *D'* show the results of similar tests with natural barley from the agricultural experiment stations of Nebraska, Wisconsin, and Kansas, respectively, while those marked *B*, *C*, and *D* are from the same stations, but have, respectively, 50 per cent, 25 per cent, and 2½ per cent of sulphured barley added.

The contrast between the precipitate in the two bottles of each pair is readily apparent. The lead sulphid is so abundant in *A*, which represents a commercially sulphured sample, that the whole solution



FIG. 3.—Seven bottles filled with solutions, showing the results of tests of samples containing different percentages of sulphured barley and of samples of natural, or unsulphured, barley from the agricultural experiment stations of Nebraska, Wisconsin, and Kansas.

is black and opaque. The solutions in *B*, *C*, and *D* vary from black turbidity to dull translucency, depending upon the percentage of sulphured barley. Contrasted with the natural barley in each case, the turbidity is very evident, and it is plainly seen that this turbidity decreases from right to left, or as the percentage of sulphured admixture decreases. Numerous other trials were made with sulphured and unsulphured grain, and in each case the same results were obtained.

Approved:

JAMES WILSON,

*Secretary of Agriculture.*

WASHINGTON, D. C., *October 12, 1909.*

[Cir. 40]